Variational quantum Monte Carlo computation of the ground state of the Helium atom

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Abstract: A computation of the ground state energy of the Helium atom has been carried out. The computation of the energy is done using the metropolis algorithm combined with a minimization algorithm and it is based on the quantum variational method. Agreement of the ground state energy with both the theoretical predictions and other numerical simulations has been found.

I. INTRODUCTION

Our final goal in this project is finding the ground state energy of the Helium atom. To this end, we will make use of a very well known computational method, the Monte Carlo method, in order to compute the integrals that are needed to obtain the average value of the observable magnitudes of the system, in particular, the energy. This method is based on, rather than performing the integral summation homogeneously over the degrees of freedom of the system, importance sampling the integrals according to a non-uniform probability density. [1] This method enables us to compute the ground state of any system by means of the quantum variational method. This method has been used first to compute the ground state energy of the Hydrogen atom and eventually the ground state energy of the Helium atom. The results obtained are discussed in the results section and compared to values found in literature.

II. THEORETICAL BACKGROUND

The variational method is a widely known method used to estimate ground states of quantum systems. [2] However, if the degrees of freedom of the system increase, performing the integral associated with the expected value of the Hamiltonian can become very challenging. Using the Monte Carlo method, specifically, the metropolis approach, we can efficiently compute the following integral via random sampling.

$$E(c) = \frac{\int d\vec{r}\psi_T^*(\vec{r},c)\hat{H}\psi_T(\vec{r},c)}{\int d\vec{r}\psi_T^*(\vec{r},c)\psi_T(\vec{r},c)} \tag{1}$$

To this end, we need to know the expression of the local energy, given our test wavefunction ψ_T. Then, the integral will read

$$E(c) = \frac{\int d\vec{r}\psi_T^*(\vec{r},c)\psi_T(\vec{r},c)E_{loc}(\vec{r},c)}{\int d\vec{r}\psi_T^*(\vec{r},c)\psi_T(\vec{r},c)} \tag{2}$$

with

$$E_{loc}(\vec{r},c) = \frac{\hat{H}\psi_T(\vec{r},c)}{\psi_T(\vec{r},c)} \tag{3}$$

In this work, we will use trial wavefunctions with a single variational parameter c. Both of the test wavefunctions (for the Hydrogen and the Helium case) and the rest of the analytical calculations required for the algorithm will be derived in the following.

For the Hydrogen case we will be using the normalized function

$$\psi_T(x,y,z,c) = \sqrt{\frac{c^3}{\pi}}e^{-cr} \tag{4}$$

with $r = \sqrt{x^2+y^2+z^2}$. Using the following Hamiltonian (in Hartree atomic units)

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{5}$$

we obtain the local energy expression

$$E_{loc}(c) = -\frac{1}{2}c^2 + \frac{c}{r} - \frac{1}{r} \tag{6}$$

For the Helium case we will be using the normalized function

$$\psi_T(x_1,y_1,z_1,x_2,y_2,z_2,c) = e^{-2r_1}e^{-2r_2}e^{\frac{r_{12}}{2(1+cr_{12})}} \tag{7}$$

with $r_i = \sqrt{x_i^2+y_i^2+z_i^2}$ and $r_{12} = |r_1 - r_2|$, $i = \{1,2\}$. Using the following Hamiltonian (in Hartree atomic units)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{8}$$

we obtain the local energy expression

$$E_{loc}(c) = -4 + (\hat{r_1} - \hat{r_2})(\vec{r_1} - \vec{r_2})\frac{1}{r_{12}(1+cr_{12})^2} - \frac{1}{r_{12}(1+cr_{12})^3} - \frac{1}{4(1+cr_{12})^4} + \frac{1}{r_{12}} \tag{9}$$

using $\vec{r_i} = (x_i, y_i, z_i)$ and $\hat{r_i} = \frac{\vec{r_i}}{r_i}$, $i = \{1,2\}$.

Furthermore, for the minimization algorithm, we will need the analytical expression of $\frac{\mathrm{d}\ln(\psi_T)}{\mathrm{d}c}$. This will obviously be different for both wavefunctions for Hydrogen and Helium. The corresponding expressions are

$$\frac{\mathrm{d}\ln\psi_T(\vec{r},c)}{\mathrm{d}c} = \frac{3}{2c} - r \tag{10}$$

and

$$\frac{\mathrm{d}\ln\psi_T(\vec{r_1},\vec{r_2},c)}{\mathrm{d}c} = \frac{-r_{12}}{2(1+cr_{12})^2} \tag{11}$$

for Hydrogen and Helium wavefunctions respectively.

Finally, we will go through the metropolis algorithm and the minimization algorithm that we will implement in order to obtain the minimum energy associated with the ground state of the considered systems according to the variational method. The flow of the algorithm follows these steps [3]:

1. We evaluate equation (2) sampling the local energy over the probability density $\rho(\vec{R}) = \frac{\psi_T^2(\vec{R})}{\int d\vec{R}'\psi_T^2(\vec{R}')}$ (in this algorithm $\vec{R}$ contains all the k degrees of freedom coordinates, it is a k entries vector). The reader may note that here we further assumed that (chosen) ψ_T is real. To do this we use the metropolis algorithm:

   (a) We put N walkers in random positions (R_i) in the degrees of freedom space ($i = 1, \ldots, N$).

   (b) We propose a shift each walker i to a new random position (R_i') by moving it inside a cube with chosen dimensions (this way detailed balance condition [1] is satisfied).

   (c) We calculate $p = \frac{\psi_T^2(\vec{R})}{\psi_T^2(\vec{R}')}$.

   (d) If $p < 1$ the new positions R_i' are accepted with probability p and if $p > 1$ the new positions R_i' are always accepted.

   (e) Finally, we store the value of the local energy (this way we end up with an array of energy measurements performed by each walker) and go to step (a), repeating the process a chosen number *iterations* of times.

2. We compute the expected value of the energy and the variance performing a mean over all measured values.

3. We repeat the two previous steps aiming to compute $< E_{loc}\frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c} >$ and $< \frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c} >$ in place of the energy $< E_{loc} >$ (this is analogous to say that we run the metropolis algorithm again using the same probability distribution and changing the local energy E_{loc} for the product $E_{loc}\frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c}$ and $\frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c}$).

4. We compute the new value of $c_{new} = c_{old} - \gamma\left(\frac{\mathrm{d}E}{\mathrm{d}c}\right)_{old}$ using $\left(\frac{\mathrm{d}E}{\mathrm{d}c}\right) = 2\left(\left\langle E_{loc}\frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c}\right\rangle - \langle E_{loc}\rangle\left\langle\frac{\mathrm{d}\ln\psi_T}{\mathrm{d}c}\right\rangle\right)$ (γ is a free parameter we can choose to enhance the performance of convergence of the method).

5. We go to step 1. and repeat the whole process again until we reach the minimum value of c according to some convergence criteria. With this value we can call step 3. to estimate the expected value of the energy and the variance associated to it.

III. DESCRIPTION OF THE COMPUTER EXPERIMENTS

In this section a description about how we carried out the simulation will be done. Namely, we will split this discussion into three parts, the first one giving details about how our computer experiment setup was built and the other ones discussing the correctness of the code and the performance of our simulations. The project principally consists of two files of code, a `functions.py` file and `week#.py` file (used to execute the computations as a `.ipynb` file), which are self explanatory regarding their content. A weekly tracing journal was also filled up while constructing the project, available in the **Gitlab repository of the project** along with the rest of the documents.

III.A. Construction of the code

In this subsection we will give some important details about the workflow in our project, in accordance with the three weeks journal we wrote when carrying it out.

1. Week 1

In *Week 1* we first set up the metropolis algorithm for the computation of the expected value integral for the energy. This algorithm can be found in `metropolis_hydrogen`. Later, this function is called in `hydro_opt` in order to minimize the variational parameter c when the full Monte Carlo algorithm was implemented. In this stage of the code, the variance computed as associated statistical error of the energy was also computed but no correlation between same walker positions was taken into account yet. The fact of constructing Monte Carlo computation for the analytical case of Hydrogen has been basically done to check the correctness of our approach. The expected results are the ones given by the analytical calculations [2][4][5], which can also be found in literature and also by literature preforming a similar computational calculation. [3]

Within this week we also made the appropriate conversions to the expressions we used such that every magnitude ended up to be expressed in Hartree atomic units, as we previously mentioned. Since we have four fundamental units in our expressions, four changes were needed to be made. The units used in the code have been written in terms of $a_0, e, \hbar$ or m_e or a combination of these. Below we show the values of these magnitudes.

$$a_0 = 5.29 \times 10^{-11}\,\mathrm{m} \tag{12}$$

$$e = 1.602 \times 10^{-19}\,\mathrm{C} \tag{13}$$

$$m_e = 9.109 \times 10^{-31}\,\mathrm{kg} \tag{14}$$

$$\hbar = 1.055 \times 10^{-34}\,\mathrm{J\,s} \tag{15}$$

We will call the dimensionless parameters with a tilde (the ones we use in our computer program), so we can after express them in SI units. For instance, we will do this for the distance and the energy, but any other magnitude is analogous.

$$r = \tilde{r} \times a_0 \tag{16}$$

$$E = \tilde{E} \times m_e c^2 \alpha^2 = \tilde{E} \times E_h \tag{17}$$

Here, E_h is defined as the Hartree energy and has a value of $E_h = 27.211\,eV$ and α is the fine structure constant, which can be written in the SI according to the following expression.

$$\alpha = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c} \tag{18}$$

The parameter ε_0 has a value of $8.854 \times 10^{-12}\,\mathrm{Fm}^{-1}$ and α in Hartree atomic units reads $\alpha = c^{-1}$, therefore making the energy expression self contained within our new units system.

2. Week 2

In *Week 2*, as we discuss in the journal of the project, we modified the code such that all the degrees of freedom in the metropolis integral calculation are merged and more than a single walker is accepted. Again, the code was run for the Hydrogen atom ground state and the expected results were expected to be the same ones we obtained in our first approach, provided the no mistake was made during the implementation.

These changes were made to make the final implementation for the helium atom much simpler. For instance, if our code goes from being able to support 3 degrees of freedom to an arbitrary number of them, the higher dimension cases (i.e. the Helium case) will be immediate to call using the same function. Specifically, given these changes, the only thing that was missing to go from the Hydrogen case to the helium case was to change the wavefunction shape and the associated other particular functions related to it.

3. Week 3

Finally, *Week 3* was focused on upgrading the code such that we are able to obtain correctly presentable results (i.e. taking into account the correlation of measurements of the same walker and the statistical error associated to the average measurement) and rewriting the code for the computation of the ground state energy of the Hydrogen atom to the ground state of the Helium atom. First, the autocorrelation function was adapted to the code. The autocorrelation function is a general function, meaning that if provided with a set of energies (or anything else) generated by different configurations (iterations) and different walkers, it can calculate the mean energy and variance no matter which system these energies correspond to. Thus, it can be used both for the Hydrogen and the Helium atom, we just have to generate the set of energies using the correspondingly adjusted metropolis algorithms.

After that, the migration to the Helium case was finally done. After correcting the wavefunction to the new case, the simulation could be run efficiently when the parameters were adjusted such that the acceptance ratio of the metropolis algorithm was about 50%. Also, as an additional note, the variance we computed was obtained following two different approaches: `variance1` corresponding to the variance over all different configurations (for different steps and different walkers), while `variance2` computes the variance between the mean energies each walker computes. Analogously with the Hydrogen case, the functions `helium_opt1` and `helium_opt2` were created to reach the minimum value of the variational parameter c (taking into account correaltion). The autocorrelation functions that compute the variance of a statistical measurement according to the two previously commented ways are `autocorrelation1` and `autocorrelation2` respectively. It is also interesting to observe the different behaviours between these two different approach's results

III.B. Code check

Given that the migration from the Hydrogen simulation to the Helium simulation is rather simple, the correctness of the code was performed via the analysis of the results obtained for the analytical Hydrogen case. Although we will discuss the results in more detail in the corresponding results section, we can slightly comment about our findings.

After having the complete simulation for the Hydrogen ground state we obtained results very similar to the ones given in the literature, both in terms of the value of the ground state energy itself and the computed (correlated) variance. [3] That enabled us to think that the implementation carried out so far was indeed correct. To check the final version of the code we also relied on comparing our values to the literature. The main sources we compared from indeed agreed that our value was a good estimation of the ground state of Helium. [3][4] However, our results for the variance observed did not match the ones obtained in the literature.

III.C. Code performance

In this section several technical details about the code will be discussed. Fist of all, the computations of the

energies have been carried out trying recreated the way it is done in [3] pg. 402. This is, the number of iterations set to 30000 and the first 4000 not taken into account when computing the mean value of the energy because of wanting to ensure equilibrium before taking real samples. However, instead of using 400 the maximum amount of walkers we used were 20.

Another technicality that is worth mentioning is the convergence criteria of the minimization loop of the c parameter. This convergence relies on minimizing the value of the variance in each mean measurement. This can be checked in the `while` loop inside the `hydro_opt` and the `helium_opt2` functions. The reader may note that sometimes the `while` loop never converges for the convergence condition but for the maximum amount of loops supported by the function ($n = 100$ for Hydrogen and $n = 40$ for Helium). In practice this does not suppose any problem because the maximum number of loops is chosen such that the value of c safely correctly converges This is due to the fact that the convergence criteria is sometimes difficult to fulfill given that the increases/decreases in the variance can be extremely small (the variance around the minimum value of the energy is very flat as a function of the variational parameter). Also, a new metropolis run can be done after finding the approximate minimum value of c to finally recover a very good approximation of the ground state energy.

The time it takes to complete the final version of the `week3.py` file is of the order or an hour. Obviously, the most time consuming part of the simulation is doing the convergence into the minimum value of c, and the simulation strongly depends on the amount or walkers used. However, since the probability densities we are using in this case do not contain regions of high probability in the configuration space which are separated by impenetrable regions of low probability, one single walker is a very wise choice for this case. Accordingly, increasing the amount of walkers for our computations has not lead into observing any improvement in terms of precision in our results.

IV. RESULTS

In this section we will present the results that we obtained through our simulation and will compare them with the values found in the literature. On the one hand, the results for the hydrogen case when using $c = 1$ give us an exact energy of

$$E = \frac{1}{2} E_h \tag{19}$$

which coincides with all the theoretical values [2] [4] [5]. The computed variance associated with the mean value obtained is identically equal to zero, which coincides with the findings or [3] and makes sense given that the shape of the wavefunction used is exactly equal to the one corresponding to the Hydrogen's electron, therefore giving no deviance in the statistical measurement.

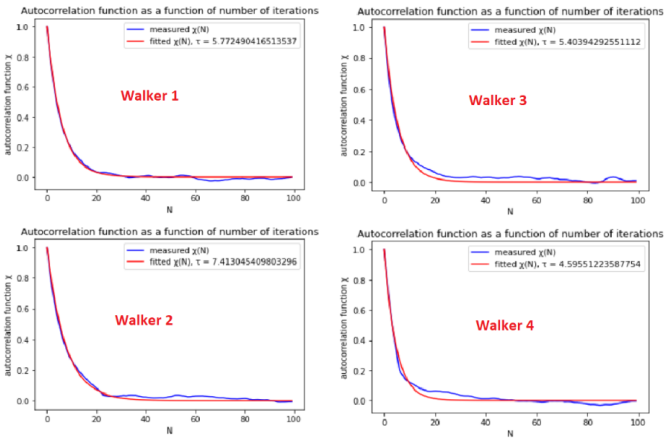

Figure 1: Autocorelation function (as a function of the iteration step) and autocorrelation times for 4 of the walkers used for the $c = 1.1$ Hydrogen (5 walkers) energy computation.

When we start from a value of the parameter c different than 1, the convergence to the correct value was also observed. Namely, starting with $c = 1.2$, the convergence of the method is given by the table below (Table I). This same calculation has been performed varying the value of γ in the convergence loop (which only affects to the convergence time if the initial guess of the parameter is very far away from the target one) and starting from different values of c. The result was similar in all cases. A single and multiple walkers were also used to compute the final value of the minimum c. No observed differences either in the convergence or the final minimal value have been observed, even though for multiple walkers the computation time raised substantially.

Table I: Minimization algorithm convergence with $c_{ini} = 1.2$ for the Hydrogen case. Ground state energy and variance of the energy measurement displayed.

c	**E** (E_h)	**Variance** (E_h^2)
1.2	$-0.5(6)$	0.3
1.007	$-0.49(9)$	0.007
1.00002	$-0.499(5)$	0.00002

The results for some initial guesses of c, only running the metropolis algorithm given those, have also been computed in order to compare them with the results extracted in [3]. For $c = 1.1$ the energy was found to be $E = -0.49(5)\, E_\mathrm{h}$ (i.e. Variance $= 0.002$). This value was found to be approximately one order of magnitude more accurate than the result obtained in the above-mentioned literature. Similarly, for $c = 0.9$, $E = -0.49(4)\, E_\mathrm{h}$ has been found, for which the variance coincides more accurately with the result found in the literature. The autocorrelation function is plotted for the $c = 1.1$ case and we observe that the correlation of the measures of the energy performed by a single walker have a correlation

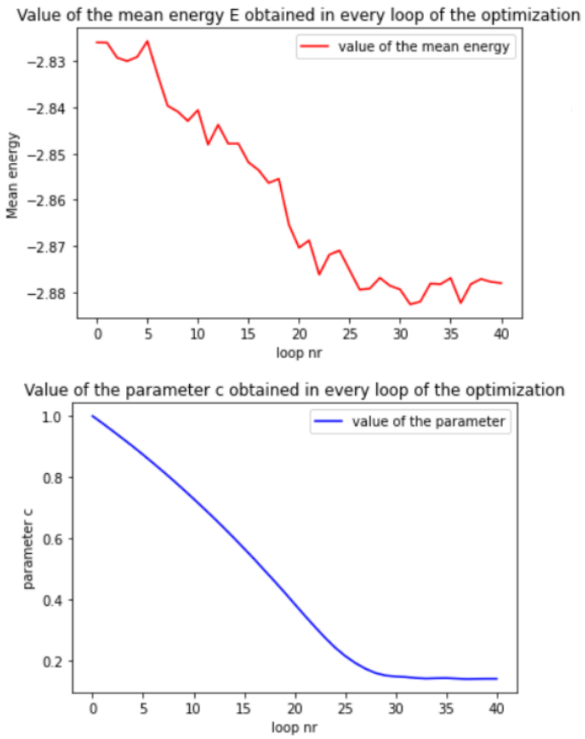

Figure 2: Top panel shows the evolution of the energy (in units of E_h) along the minimization algorithm for the Helium case, that is, as a function of the loop number. Bottom panel shows the same behaviour for the c value in the y axis.

of approximately 6 time steps. Plot for the 4 (out of 5) walker's correlation function is shown in Figure 1. The reader must note that so far we have only displayed results with variance computed according to the second method stated (i.e. using `helium_opt2` which computes variance labelled as `variance2` in III III.A 3).

Table II: Metropolis energy computation for several values of the variational parameter c. Ground state energy and variance of the energy measurement displayed.

c	**E** (E_h)	**Var** (E_h^2)
0.05	−2.87(9)	0.009
0.075	−2.88(9)	0.008
0.1	−2.88(9)	0.008
0.125	−2.87(8)	0.007
0.15	−2.87(8)	0.007
0.175	−2.88(8)	0.007
0.2	−2.88(8)	0.007
0.25	−2.88(9)	0.008

On the other had, the most important results, regarding the Helium atom, will be discussed. Analogously to the Hydrogen case, we started computing single metropolis energy calculations for a given value of the variational parameter c. The results (again only for the correlated data approach) can be seen in Table II. Comparing our results to the ones obtained in [3], we can tell that the results are very similar, although the variance obtained in our approach is one order of magnitude smaller. This makes that our computation of the ground state energy is reliable more accurately. For both approaches the value of the variational parameter that minimizes the enrgy is found to be $c = 0.175$ and the estimation of the ground energy of the Helium atom is thus $E = -2.88(8)\, E_\mathrm{h}$.

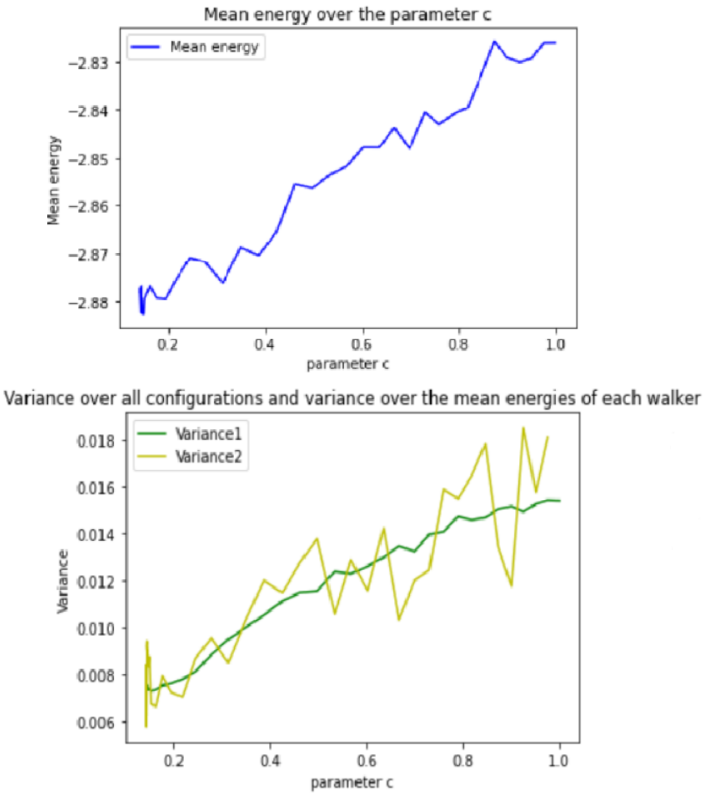

Figure 3: Top panel shows the evolution of the energy (in units of E_h) as a function of the variational parameter c for the Hydrogen case, obtained from the minimization algorithm. Bottom panel shows the same behaviour for the variance of the energy (in units of E_h^2) in the y axis.

If we go now to the whole minimization algorithm, we expect to find it to converge around that c value previously stated. Indeed, the findings give support to our previous result. The minimization algorithm is set to start at $c = 1$ and is left to evolve with a factor $\gamma = 0.5$ during a maximum of 40 steps. The convergence of the variational parameter can and the evolution of the computed energy can be found in Figure 2. Furthermore, the ground state energy and both computations of the variance as a function of c can also be found in Figure 3, where a similar behaviour can be seen regarding their trend.

In Figure 2 we can indeed see that the convergence of the parameter c goes towards $c \approx 0.175$ and stabilizes very near that value, as expected. We can also see that indeed a maximum of 40 iterations is enough to make sure convergence given our initial parameter value and

the γ factor used. The energy also stabilizes around $E = -2.88\,E_\mathrm{h}$ which is found within the error of the value previously shown.

Figure 3 shows in a clearer fashion how the energy is minimized as a function of the variational parameter and how the variance also minimizes around the zone $c \approx 0.175$. After running a last metropolis step given the final value of c in the minimization algorithm we obtain as a result of the ground state energy of the Helium atom

$$E = -2.88(8)\,E_\mathrm{h} \tag{20}$$

which corresponds to a variance value observed of

$$Var(E) = 0.08\,E_\mathrm{h}^2 \tag{21}$$

Evidently, this results agrees with the previous approach and it also agrees with the values given by literature. [2] [4] [5] Specifically, the accuracy of our results is obtained to be better than *First order perturbation* and *Simple variational* theoretical approaches shown in [4], and correctly within the error bar compared to the *Exact* value given in that same reference.

V. CONCLUSIONS

We have been able to estimate with great precision the value of the ground state energy of the Helium atom. Our findings have been compared to theoretical computations as well as other numerical computations and agreement is found in all of the computations. Our approach gives more accuracy than using the simple first order in perturbation theory or using the analytical variational method.

In terms of increasing the precision and speed of our method, several approaches have been tested. Increasing the number of walkers was not found to give any enhancement in terms of the precision of the final result although it notably increased the computational time. The use of a single walker for this specific problem does not suppose a problem given that the probability function we intend to sample in is not irregularly lumped with high probability isolated regions. Factor γ was also varied in order to see the differences in computation times. Convergence from a far-to-target initial value of c is observed to be faster but convergence is found to be harder. Thus, a good further approach would be to reduce the γ factor on the fly during the convergence of c. Only one variational parameter minimization was studied, although an implementation for a second one would be straight-forward. Minimization process could be implemented by brute force or other already existing algorithms.

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